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THERMAL ANALYSIS OF COMPLEX FLUORIDES

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A number of fluorometallates has been investigated by thermal analysis to establish the decomposition stoichiometry and to determine the conditions where stable intermediate phases can be isolated. The decomposition reactions of fluorovanadates depend on the atmosphere. For ammonium hexafluorometallates and potassium pentafluoroaquametallates the decomposition temperatures or enthalpies can be correlated to crystal field stabilization energies.

Thermal analysis has found very wide application in coordination chemistry. A number of neutral complexes have been investigated to get a correlation between the thermal stability of the solid compounds and their formation constants in the solution [1]. On the other hand the anionic complexes such as oxalates have been studied as precursor compounds in the preparation of simple and complex oxides [1]. We are interested in the synthesis of fluorides and fluorometallates so we studied a number of decomposition reactions, which could give us stable intermediate phases as well as final metal fluorides. We also tried to find some correlations between the decomposition reactions and the structural characteristics of the fluoro complexes.

Taking a group of $(NH_4)_3MF_6$ compounds with M = Al, Ga, In, Sc,Ti, V, Cr, Mn, Fe a stepwise decomposition could be expected giving intermediate phases according to the following reaction:

$$(NH_4)_3MF_6 \rightarrow (NH_4)_2MF_5 \rightarrow NH_4MF_4 \rightarrow MF_3$$

However, only for Mn the intermediate $(NH_4)_2MnF_5$ has been isolated [2].

Mostly investigated ammonium fluorometallate is $(NH_4)_3AlF_6$ (Fig. 1) with the decomposition scheme [3, 4]:

$$(NH_4)_3AlF_6 \rightarrow NH_4AlF_4 + 2\,NH_4F$$

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$$NH_4AlF_4 \rightarrow \gamma\text{-}AlF_3 + NH_4F$$

$$\gamma\text{-}AlF_3 \rightarrow \alpha\text{-}AlF_3.$$

NH_4AlF_4 can be isolated isothermally at temperatures between 170 and 220°. It seems to be a multistage decomposition of NH_4AlF_4 with the intermediate compositions of $AlF_3 \cdot xNH_4F$ (x = 0.1 - 0.2) and $AlF_3 \cdot yNH_4F$

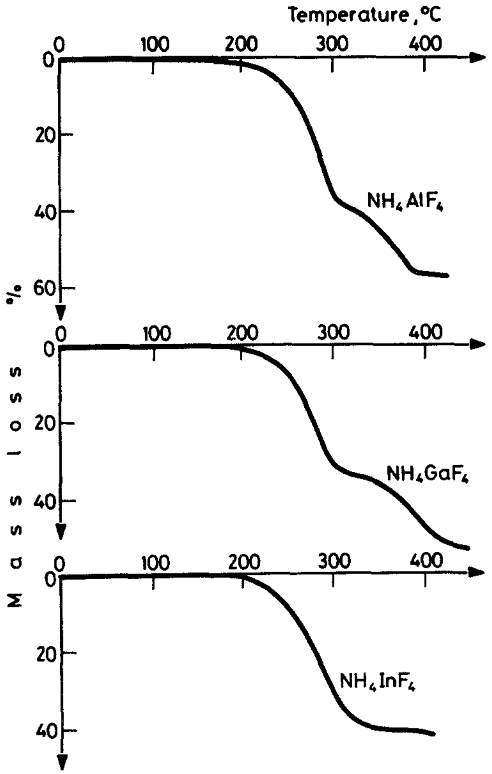

Fig. 1 TG curves of $(NH_4)_3MF_6$, M = Al, Ga, In in argon

(y = 0.04-0.06), which can be differentiated by X-ray powder diffraction [4].

$(NH_4)_3GaF_6$ behaves similarly to $(NH_4)_3AlF_6$ and decomposes according to the following scheme [3]:

$$(NH_4)_3GaF_6 \rightarrow NH_4GaF_4 + 2\,NH_4F$$

$$NH_4GaF_4 \rightarrow \gamma\text{-}GaF_3 + NH_4F$$

$$\gamma\text{-}GaF_3 \rightarrow \alpha\text{-}GaF_3$$

The temperature of 170°, for isothermal isolation of NH_4GaF_4 is even lower as that one for NH_4AlF_4. Pure γ-GaF_3 can be prepared by isothermal weight loss already at 250°.

The third hexafluorometallate from this group is $(NH_4)_3InF_6$ which has somewhat different TG and DTA curves as the previous two compounds [3], the reactions however are the same:

$$(NH_4)_3InF_6 \rightarrow NH_4InF_4 + 2\,NH_4F$$

$$NH_4InF_4 \rightarrow InF_3 + NH_4F$$

$(NH_4)_3InF_6$ gives NH_4InF_4 at 170° at isothermal conditions. At 180° already, a stable phase with the composition. $InF_3 \cdot 0 \cdot 3NH_4F$ could be isolated, however with X-ray powder pattern of InF_3 and NH_4InF_4.

The first row transitions elements show more diversity in the decomposition reactions of $(NH_4)_3MF_6$ compounds [5] (Fig. 2). The TG and DTA curves of $(NH_4)_3ScF_6$ look the same as those of $(NH_4)_3InF_6$ and give no information on the intermediate phases. In isothermal experiments NH_4ScF_4 could be isolated at 130° within a few weeks, at 150° already the reaction continues slowly giving ScF_3. The decomposition scheme is:

$$(NH_4)_3ScF_6 \rightarrow NH_4ScF_4 + 2\,NH_4F$$

$$NH_4ScF_4 \rightarrow ScF_3 + NH_4F$$

$(NH_4)_3TiF_6$ has two polymorphic transitions, the first at 35 and the second at 100°. The TG curve indicates two intermediate phases, however only NH_4TiF_4 could be isolated isothermaly at 170°. The decomposition of NH_4TiF_4 is accompanied also by the sublimation of undecomposed substance. The reactions are:

$$(NH_4)_3TiF_6 \rightarrow NH_4TiF_4 + 2\,NH_4F$$

$$NH_4TiF_4 \rightarrow TiF_3 + NH_4F$$

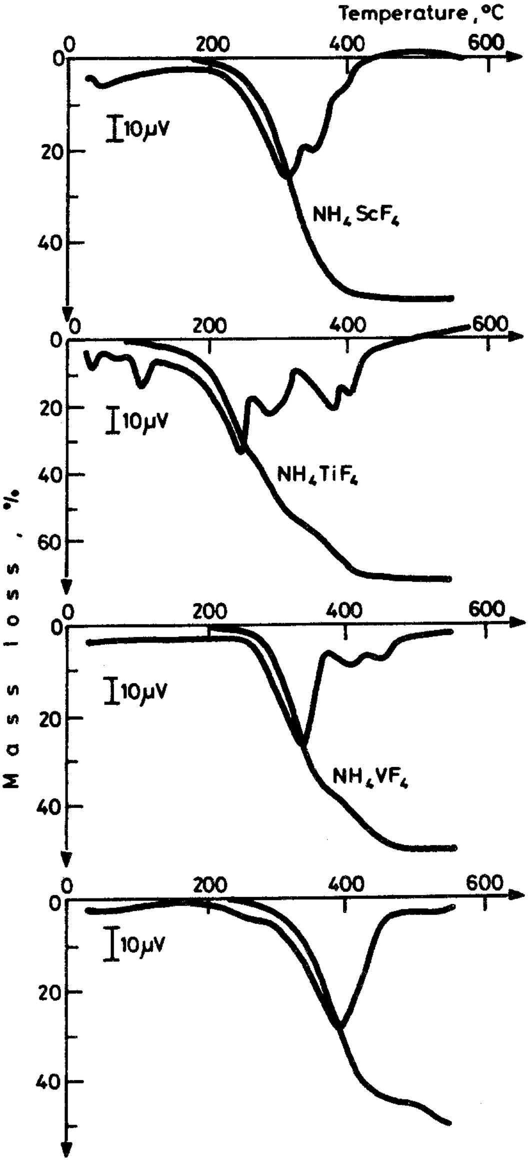

Fig. 2 TG and DTA curves of $(NH_4)_3MF_6$, M = Sc, Ti, C, Cr in argon

According to the decomposition reactions $(NH_4)_3VF_6$ resembles to the previous compounds but from the dynamic measurements there is not much similarity between the last three fluorometallates [5]. Isothermaly again NH_4VF_4 could be isolated at 170° and the reaction is:

$$(NH_4)_3VF_6 \rightarrow NH_4VF_4 + 2\,NH_4F$$

$$NH_4VF_4 \rightarrow VF_3 + NH_4F$$

Thermal decomposition of $(NH_4)_3CrF_6$ begins at higher temperature as previous compounds and goes directly to CrF_3 without any intermediate phases, so the reaction is:

$$(NH_4)_3CrF_6 \rightarrow CrF_3 + 3NH_4F$$

The next element, the manganese, is also an exception because all theoretically possible compounds $(NH_4)_3MnF_6$, $(NH_4)_2MnF_5$ and NH_4MnF_4 can be prepared from aqueous solution of the corresponding fluorides [6]. The TG curve of $(NH_4)_3MnF_6$ (Fig. 3) does not permit the establishment of the stoichiometry of the decomposition reactions [2]. The same can be said for $(NH_4)_2MnF_5$. For NH_4MnF_4 the departure of NH_4F is accompanied by the reduction of manganese giving MnF_2 at the end of the reaction. According to isothermal mass loss determination the reactions are:

$$(NH_4)_3MnF_6 \rightarrow (NH_4)_2MnF_5 + NH_4F$$

$$(NH_4)_2MnF_5 \rightarrow NH_4MnF_4 + NH_4F$$

The last reaction depends on the atmosphere used. In an inert and in an oxidative atmosphere respectively, the reactions are:

$$3NH_4MnF_4 \rightarrow 3MnF_2 + 1/2N_2 + 2\,NH_3 + 6HF$$

$$NH_4MnF_4 + \tfrac{1}{2}O_2 \rightarrow MnF_2 + \tfrac{1}{2}N_2 + 2\,HF + H_2O$$

Additionally a polymorphic transition to a high temperature cubic form of $(NH_4)_3MnF_6$ has been detected at 92°.

Iron again behaves as the most elements with the following decomposition scheme [7]:

$$(NH_4)_3FeF_6 \rightarrow NH_4FeF_4 + 2NH_4F$$

$$NH_4FeF_4 \rightarrow FeF_3 + NH_4F$$

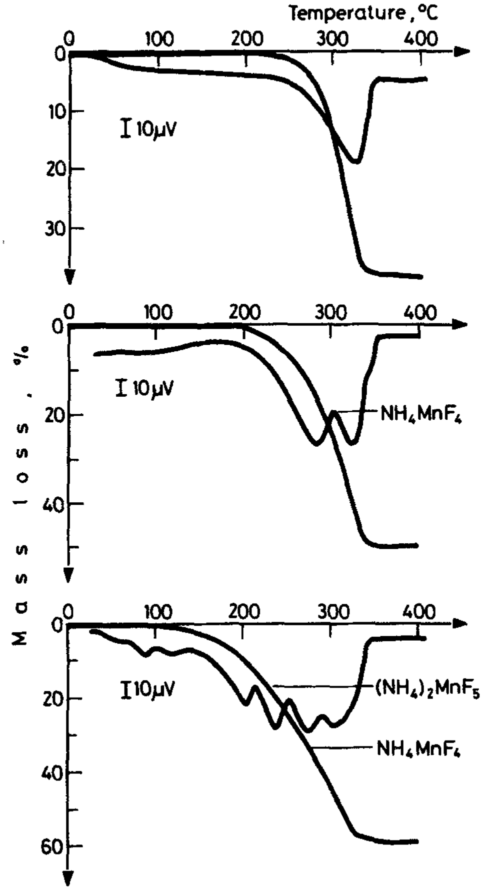

Fig. 3 TG and DTA curves of NH_4MnF_4, $(NH_4)_2MnF_5$ and $(NH_4)_3MF_6$ in argon

For $(NH_4)_3MF_6$ type of compounds the TG curves can obviously not be used to predict the reaction pathway. There are only isothermal measurements at low enough temperatures which can give the answer to these questions. There is no detailed analysis of decomposition enthalpies and/or activation energies which could give some explanation of the differences mentioned. Anyway, much higher stability of $(NH_4)_3CrF_6$ which causes the complex to decompose directly to CrF_3 can be explained by high crystal field stabilization energy for octahedral d^3 configuration. The exceptional position of manganese compounds e.g. the occurrence of all possible intermediate phases and lower decomposition temperature of $(NH_4)_3MnF_6$ could probably be ascribed to Jahn-Teller effect.

Thermal decomposition of ammonium fluorooxovanadates(IV), $(NH_4)_3VOF_5$, $(NH_4)_2VOF_4$ and $(NH_4)_2VOF_4 \cdot H_2O$ has been studied in inert and in oxidative atmosphere [8] (Fig. 4). On the TG curves of these compounds the intermediate phases are indicated which were isolated in isothermal experiments. In both atmospheres the decomposition reactions are:

$$(NH_4)_3VOF_5 \rightarrow \mathrm{HT}\ (NH_4)_3VOF_5 \rightarrow (NH_4)_5V_3O_3F_{14} \rightarrow (NH_4)_2VOF_4 \rightarrow NH_4VOF_3$$

$$(NH_4)_2VOF_4 \cdot H_2O \rightarrow (NH_4)_2VOF_4 \rightarrow NH_4VOF_3$$

Further decomposition of NH_4VOF_3 depends on the atmosphere:

$$NH_4VOF_3 \rightarrow VF_3 + \mathrm{V(III)oxide}$$

$$NH_4VOF_3 + O_2 \rightarrow VOF_3 \rightarrow V_2O_5$$

With bigger cations, such as NMe_4 or NEt_4 the following fluorooxovanadates(IV) have been prepared and studied by thermal analysis:
$[NMe_4]_2[V_2O_2F_6(H_2O)_2]$, $[NEt_4]_2[V_2O_2F_6(H_2O)_2]$, $[NEt_4][V_2O_2F_5(H_2O)_3]$ [9, 10]. The only intermediate phases that could be isolated were anhydrous complexes. The final products were again impure VF_3 in an inert atmosphere and V_2O_5 in the air.

Classical amine complexes with anions other than fluoride belong to the compounds studied most extensively. $[Co(NH_3)_6]X_3$ where X = Cl, Br, I decompose through several steps to give CoX_2 as a final product [11, 12]. For X = F quite different intermediate phases were detected [13], namely $[Co(NH_3)_5F]F_2$, $[Co(NH_3)_4F_2]F$ and $[Co(NH_3)_3F_3]$. Thermal decomposition of $[Co(NH_3)_6]MF_6$ with M = Al, Ga, In, Sc, Ti, V, Cr, Mn, Fe show also interesting stoichiometry [14]. The complexes $[Co(NH_3)_6]MF_6$ M = Sc, Mn decompose directly to give mixtures $CoF_2 + ScF_3$ and $CoF_2 + MnF_2$ respectively. In the course of the decomposition only a mixture of initial complex and final fluorides could be identified. The compounds with M = Al, Ga, V, Cr, Fe all decompose in two steps. The reactions are:

$$6\,Co(NH_3)_6MF_6 \rightarrow 6NH_4CoMF_6 + N_2 + 28NH_3$$
$$NH_4CoMF_6 \rightarrow CoF_2 + MF_3$$

for M = Al, Ga, V, Cr and

$$NH_4CoFeF_6 \rightarrow CoF_2 + FeF_2$$

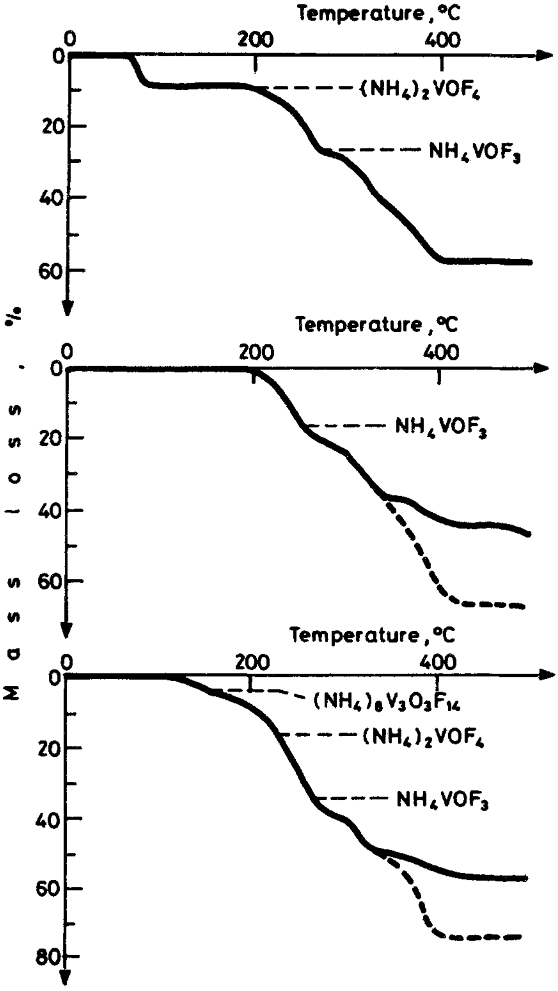

Fig. 4 TG curves of $(NH_4)_2VOF_4\cdot H_2O$, $(NH_4)_2VOF_4$ and $(NH_4)_3VOF_5$ in argon (—) and in air (- - -)

In the first reaction Co(III) reduces to Co(II) to yield cubic intermediate phases which are isostructural to a series of compounds $M^IM^{II}M^{III}F_6$ already known for M^I =alkali metals [15]. The cell parameters are summarized in Table 1.

Table 1 Cell parameters for NH_4CoMF_6 compounds

Compound	*a*, Å
NH_4CoAlF_6	10.052(2)
NH_4CoGaF_6	10.2702(5)
NH_4CoVF_6	10.387(1)
NH_4CoCrF_6	10.295(5)
NH_4CoFeF_6	10.4151(5)

Further decomposition of NH_4CoMF_6 phases has the same pathway in all cases. The only exception is NH_4CoFeF_6 which yields a mixture of two divalent fluorides.

Thermal decomposition of $[Co(NH_3)_6]InF_6$ takes place in two stages with a mixture CoF_2 + InF_3 at the end of the reaction. No definite intermediate phase has been isolated.

One area of interest in coordination chemistry are also the hydrates, particularly the question whether the water molecules are coordinated to the metal ion or present as the lattice water. Anyway, it is an interesting question if the mode of bonding of water molecules can be determined by thermal analysis. The compounds of general formula $K_2MF_5H_2O$ belong to two structural types. For M = Al, Mn [16, 17] the MF_6 octahedra share their trans vertices to form infinite anionic chains with water molecules between them. For M = V, Cr, Fe, Ga the water molecules together with five fluorine atoms form isolated $MF_5(H_2O)$ octahedra [18, 19]. Comparison of DTA curves for the dehydration show that the reaction temperature can not be used to distinguish between the lattice and the coordination water [20]. Dehydration enthalpies for the compounds with coordination water however can be correlated with the crystal field stabilization energies for their high spin configurations.

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Zusammenfassung — Mittels Thermoanalyse wurde eine Anzahl Fluorometallate untersucht, um die Stöchiometrie der Zersetzung zu ergründen und diejenigen Bedingungen festzustellen, unter denen stabile Intermediärphasen isoliert werden können. Die Zersetzungsreaktionen von Fluorovanadaten hängen von der Atmosphäre ab. Zersetzungstemperaturen oder -enthalpien für Ammoniumhexafluorometallate und Kaliumpentafluoroaquametallate können mit Kristallfeld-Stabilisierungsenergien korreliert werden.